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Published in:
Acta Crystallographica Section E-Structure Reports Online

DOI:
10.1107/S1600536807018843

Publication date:
2007

Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-(4-Bromophenyl)-2-ethylacrylic acid

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Received 22 February 2007
Accepted 16 April 2007

Key indicators

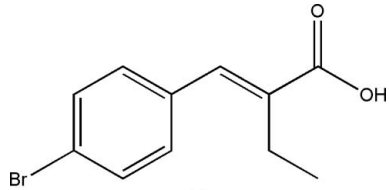
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.026
wR factor = 0.067
Data-to-parameter ratio = 18.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The configuration in the solid state structure of the title compound, $C_{11}H_{11}BrO_2$, about the C=C double bond is *E*. In the crystal structure, symmetry-related molecules are linked by O—H···O hydrogen bonds, forming centrosymmetric carboxylic acid dimers.

Comment

Cinnamic acid derivatives are used in the shikimic acid metabolic pathways of higher plants (Forgó *et al.*, 2005). These compounds are also widely used as starting materials for the synthesis of antimalarial drugs. The most active compounds in this group are halo-substituted (Nodiff *et al.*, 1971).



(I)

The molecular structure of the title compound, (I), is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The length of the C7=C8 bond [1.348 (2) Å] shows its double-bond character. The configuration about the C=C double bond is *E*. The bond lengths within the phenyl ring range from 1.382 (2) to 1.408 (2) Å, typical of aromatic character (Allen *et al.*, 1987). The Br—C3 bond distance is normal. In the crystal structure of (I), centrosymmetric dimers are formed *via* O—H···O hydrogen bonds involving the carboxylic acid groups (Fig. 2 and Table 2). The dimers are

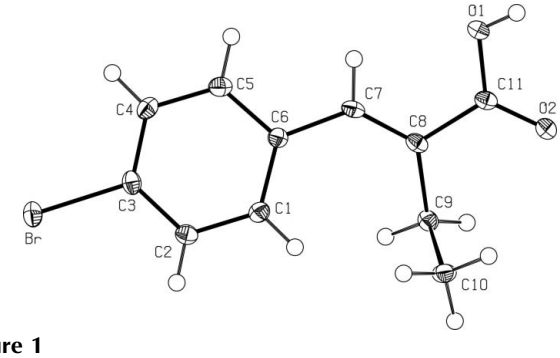


Figure 1
The molecular structure of the title compound, showing the atom numbering scheme. Displacement ellipsoids for non-H atoms are represented at the 50% probability level. The H atoms are drawn with an arbitrary radius.

further linked by C—H···O bonds, forming a sheet-like structure.

Experimental

Compound (I) was synthesized according to a previously reported method (Gensler *et al.*, 1958). A mixture of 4-bromobenzaldehyde (1.85 g 10 mmol), ethylmalonic acid (2.64 g 20 mmol) and piperidine (1.98 ml 20 mmol) in a pyridine (12.5 ml) solution was heated on a steam-bath for 24 h. The reaction mixture was cooled and added to a mixture of 25 ml of concentrated HCl and 50 g of ice. The precipitate formed in the acidified mixture was filtered off and washed with ice-cold water. The product was recrystallized from an alcohol–water mixture (4:1). The yield was 65%.

Crystal data

$C_{11}H_{11}BrO_2$
$M_r = 255.11$
Monoclinic, $P2_1/c$
$a = 11.9803$ (9) Å
$b = 5.0008$ (4) Å
$c = 16.986$ (1) Å
$\beta = 101.880$ (1)°
$V = 995.85$ (12) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.10$ mm^{-1}
$T = 100$ (1) K
0.49 × 0.39 × 0.21 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.164$, $T_{max} = 0.423$
8570 measured reflections
2461 independent reflections
2168 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.067$
$S = 1.03$
2461 reflections
132 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br—C3	1.9034 (16)	O2—C11	1.227 (2)
O1—C11	1.330 (2)		
Br—C3—C2	118.83 (12)	O2—C11—C8	121.63 (15)
Br—C3—C4	119.78 (12)	O1—C11—O2	122.22 (15)
O1—C11—C8	116.16 (14)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···O2^{i}	0.79 (4)	1.89 (3)	2.6716 (18)	172 (3)
C4—H4···O2^{ii}	0.95	2.52	3.457 (2)	167
C7—H7···O1	0.95	2.28	2.722 (2)	107

Symmetry codes: (i) $-x+1, -y+3, -z+1$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

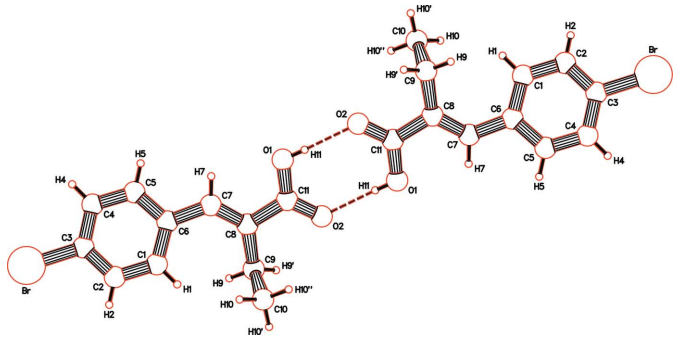


Figure 2
Perspective drawing of the dimer formed by O—H···O hydrogen bonds, shown as dashed lines.

All H atoms except H11 were included in the riding model approximation, with C—H = 0.95–0.98 and $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.5$ for methyl and $x = 1.2$ for other H atoms. Atom H11 was located in a difference Fourier map and refined freely with an isotropic displacement parameter.

Data collection: *SMART* (Bruker, 2006); cell refinement: *SAINT-Plus* (Bruker, 2006); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2006); program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLUTO* (Meetsma, 2007) and *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

NM and ZR are grateful to the Higher Education Commission of Pakistan for financial support.

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supporting information

Acta Cryst. (2007). E**63**, o2557–o2558 [https://doi.org/10.1107/S1600536807018843]

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Crystal data

$C_{11}H_{11}BrO_2$
$M_r = 255.11$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.9803$ (9) Å
$b = 5.0008$ (4) Å
$c = 16.986$ (1) Å
$\beta = 101.880$ (1)°
$V = 995.85$ (12) Å^3
$Z = 4$
$F(000) = 512$

The final unit cell was obtained from the xyz centroids of 4668 reflections after integration using the SAINTPLUS software package (Bruker, 2000).
Reduced cell calculations did not indicate any higher metric lattice symmetry and examination of the finalatomic coordinates of the structure did not yield extra symmetry elements (Spek, 1988; Le Page 1987, 1988)
$D_x = 1.695$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4668 reflections
$\theta = 2.5$–$29.7°$
$\mu = 4.10$ mm^{-1}
$T = 100$ K
Block, colourless
0.49 × 0.39 × 0.21 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine focus sealed Siemens Mo tube
Parallel mounted graphite monochromator
Detector resolution: 66.06 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)

$T_{min} = 0.164$, $T_{max} = 0.423$
8570 measured reflections
2461 independent reflections
2168 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.5°$
$h = -15 \rightarrow 15$
$k = -6 \rightarrow 6$
$l = -21 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.067$
$S = 1.03$
2461 reflections
132 parameters
0 restraints
Primary atom site location: heavy-atom method

Secondary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.5488P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	0.10293 (1)	−0.00456 (3)	0.11662 (1)	0.0179 (1)
O1	0.48650 (11)	1.2836 (3)	0.40981 (8)	0.0180 (4)
O2	0.39590 (10)	1.3078 (2)	0.51247 (7)	0.0177 (3)
C1	0.17990 (15)	0.5620 (3)	0.29802 (11)	0.0152 (4)
C2	0.12616 (14)	0.3632 (3)	0.24646 (10)	0.0153 (4)
C3	0.17875 (14)	0.2639 (3)	0.18739 (10)	0.0153 (4)
C4	0.28467 (15)	0.3581 (3)	0.17836 (11)	0.0166 (5)
C5	0.33695 (15)	0.5577 (4)	0.22982 (11)	0.0171 (5)
C6	0.28693 (13)	0.6633 (3)	0.29121 (10)	0.0136 (4)
C7	0.34837 (13)	0.8779 (3)	0.34163 (10)	0.0142 (5)
C8	0.33502 (14)	0.9728 (3)	0.41337 (11)	0.0137 (4)
C9	0.25341 (14)	0.8740 (3)	0.46371 (10)	0.0151 (5)
C10	0.14192 (15)	1.0335 (3)	0.44993 (12)	0.0188 (5)
C11	0.40807 (13)	1.2020 (3)	0.44961 (10)	0.0136 (4)
H1	0.14360	0.63037	0.33852	0.0183*
H2	0.05388	0.29637	0.25182	0.0183*
H4	0.32042	0.28747	0.13788	0.0199*
H5	0.40868	0.62513	0.22341	0.0205*
H7	0.40655	0.96284	0.32023	0.0170*
H9	0.29093	0.88527	0.52126	0.0181*
H9′	0.23562	0.68362	0.45088	0.0181*
H10	0.15885	1.22220	0.46264	0.0281*
H10′	0.09295	0.96348	0.48479	0.0281*
H10"	0.10262	1.01680	0.39354	0.0281*
H11	0.517 (3)	1.414 (7)	0.4302 (19)	0.053 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0228 (1)	0.0143 (1)	0.0161 (1)	−0.0014 (1)	0.0026 (1)	−0.0027 (1)
O1	0.0158 (6)	0.0185 (6)	0.0209 (7)	−0.0061 (5)	0.0064 (5)	−0.0031 (5)
O2	0.0177 (6)	0.0169 (6)	0.0191 (6)	−0.0045 (5)	0.0050 (5)	−0.0026 (5)
C1	0.0146 (8)	0.0158 (7)	0.0157 (8)	0.0014 (6)	0.0042 (7)	−0.0003 (7)
C2	0.0144 (7)	0.0149 (8)	0.0166 (8)	−0.0005 (6)	0.0033 (7)	0.0021 (6)
C3	0.0185 (8)	0.0115 (7)	0.0147 (8)	0.0000 (6)	0.0010 (7)	−0.0005 (6)
C4	0.0189 (8)	0.0157 (8)	0.0164 (8)	0.0026 (6)	0.0066 (7)	−0.0007 (6)

C5	0.0154 (8)	0.0176 (7)	0.0195 (9)	−0.0006 (6)	0.0063 (7)	0.0014 (7)
C6	0.0134 (7)	0.0125 (7)	0.0148 (8)	0.0003 (6)	0.0029 (6)	0.0003 (6)
C7	0.0094 (7)	0.0139 (8)	0.0191 (9)	−0.0007 (6)	0.0028 (6)	0.0024 (6)
C8	0.0100 (7)	0.0112 (7)	0.0191 (9)	0.0006 (5)	0.0011 (7)	0.0017 (6)
C9	0.0154 (8)	0.0143 (8)	0.0155 (8)	−0.0016 (6)	0.0029 (7)	0.0002 (6)
C10	0.0154 (8)	0.0178 (8)	0.0253 (10)	−0.0008 (6)	0.0094 (8)	−0.0019 (7)
C11	0.0102 (7)	0.0126 (7)	0.0176 (8)	0.0016 (6)	0.0018 (6)	0.0031 (6)

Geometric parameters (Å, º)

Br—C3	1.9034 (16)	C8—C9	1.508 (2)
O1—C11	1.330 (2)	C9—C10	1.532 (2)
O2—C11	1.227 (2)	C1—H1	0.9500
O1—H11	0.79 (4)	C2—H2	0.9500
C1—C2	1.392 (2)	C4—H4	0.9500
C1—C6	1.405 (2)	C5—H5	0.9500
C2—C3	1.382 (2)	C7—H7	0.9500
C3—C4	1.391 (2)	C9—H9	0.9900
C4—C5	1.388 (3)	C9—H9′	0.9900
C5—C6	1.408 (2)	C10—H10	0.9800
C6—C7	1.472 (2)	C10—H10′	0.9800
C7—C8	1.348 (2)	C10—H10"	0.9800
C8—C11	1.496 (2)		
Br···C1^{i}	3.7246 (18)	C2···H2^{xi}	3.0600
Br···C6^{i}	3.7042 (17)	C4···H9^{iii}	2.9800
Br···C10^{ii}	3.7221 (18)	C6···H9′	2.9000
Br···H10^{iii}	3.1600	C8···H1	2.9300
Br···H10′^{iv}	3.1900	C9···H1	2.5700
O1···C6^{v}	3.376 (2)	C10···H1	2.7700
O1···O2^{vi}	2.6716 (18)	C11···H10	3.0400
O2···C11^{vi}	3.3641 (19)	C11···H11^{vi}	2.81 (3)
O2···C9^{v}	3.3219 (19)	H1···C8	2.9300
O2···O1^{vi}	2.6715 (18)	H1···C9	2.5700
O2···C10	3.307 (2)	H1···C10	2.7700
O1···H5^{vii}	2.9100	H1···H9′	2.0200
O1···H7	2.2800	H1···H10"	2.2400
O1···H9^{viii}	2.8100	H2···C1^{xii}	2.9900
O2···H10	2.8200	H2···C2^{xii}	3.0600
O2···H9	2.4800	H4···O2^{iii}	2.5200
O2···H9′^{v}	2.7400	H4···H9^{iii}	2.5400
O2···H11^{vi}	1.89 (3)	H5···H7	2.3600
O2···H4^{ix}	2.5200	H5···O1^{xiii}	2.9100
C1···Br^{v}	3.7246 (18)	H7···O1	2.2800
C1···C9	3.180 (2)	H7···H5	2.3600
C1···C10	3.593 (2)	H9···O2	2.4800
C3···C6^{i}	3.587 (2)	H9···O1^{viii}	2.8100
C3···C7^{i}	3.539 (2)	H9···C4^{ix}	2.9800

C6···Br^{v}	3.7042 (17)	H9···H4^{ix}	2.5400
C6···O1^{i}	3.376 (2)	H9′···O2^{i}	2.7400
C6···C3^{v}	3.587 (2)	H9′···C1	2.6200
C7···C3^{v}	3.539 (2)	H9′···C6	2.9000
C8···C11^{viii}	3.564 (2)	H9′···H1	2.0200
C9···C1	3.180 (2)	H9′···H10^{i}	2.5100
C9···O2^{i}	3.3219 (19)	H10···O2	2.8200
C10···C1	3.593 (2)	H10···C11	3.0400
C10···O2	3.307 (2)	H10···H9′^{v}	2.5100
C10···Br^{x}	3.7221 (18)	H10···Br^{ix}	3.1600
C11···C11^{viii}	3.211 (2)	H10′···H10′^{xiv}	2.4200
C11···O2^{vi}	3.3641 (19)	H10′···Br^{xv}	3.1900
C11···C8^{viii}	3.564 (2)	H10"···C1	3.0500
C1···H10"	3.0500	H10"···H1	2.2400
C1···H2^{xi}	2.9900	H11···O2^{vi}	1.89 (3)
C1···H9′	2.6200	H11···C11^{vi}	2.81 (3)

C11—O1—H11	110 (2)	C6—C1—H1	119.00
C2—C1—C6	121.15 (16)	C1—C2—H2	120.00
C1—C2—C3	119.50 (16)	C3—C2—H2	120.00
Br—C3—C2	118.83 (12)	C3—C4—H4	121.00
C2—C3—C4	121.38 (15)	C5—C4—H4	121.00
Br—C3—C4	119.78 (12)	C4—C5—H5	119.00
C3—C4—C5	118.52 (16)	C6—C5—H5	119.00
C4—C5—C6	122.03 (17)	C6—C7—H7	115.00
C1—C6—C5	117.41 (15)	C8—C7—H7	115.00
C5—C6—C7	117.79 (15)	C8—C9—H9	109.00
C1—C6—C7	124.77 (15)	C8—C9—H9′	109.00
C6—C7—C8	130.13 (15)	C10—C9—H9	109.00
C7—C8—C11	118.28 (15)	C10—C9—H9′	109.00
C9—C8—C11	114.23 (14)	H9—C9—H9′	108.00
C7—C8—C9	127.49 (15)	C9—C10—H10	109.00
C8—C9—C10	112.92 (13)	C9—C10—H10′	109.00
O1—C11—C8	116.16 (14)	C9—C10—H10"	109.00
O2—C11—C8	121.63 (15)	H10—C10—H10′	109.00
O1—C11—O2	122.22 (15)	H10—C10—H10"	109.00
C2—C1—H1	119.00	H10′—C10—H10"	109.00

C6—C1—C2—C3	−0.2 (2)	C1—C6—C7—C8	18.6 (3)
C2—C1—C6—C5	0.6 (2)	C5—C6—C7—C8	−163.67 (18)
C2—C1—C6—C7	178.30 (15)	C6—C7—C8—C9	2.3 (3)
C1—C2—C3—Br	−179.19 (12)	C6—C7—C8—C11	−177.88 (15)
C1—C2—C3—C4	0.1 (2)	C7—C8—C9—C10	−95.5 (2)
Br—C3—C4—C5	178.74 (13)	C11—C8—C9—C10	84.67 (18)
C2—C3—C4—C5	−0.6 (2)	C7—C8—C11—O1	−4.2 (2)
C3—C4—C5—C6	1.1 (3)	C7—C8—C11—O2	175.82 (15)

C4—C5—C6—C1	−1.1 (3)	C9—C8—C11—O1	175.65 (14)
C4—C5—C6—C7	−178.93 (16)	C9—C8—C11—O2	−4.4 (2)

Symmetry codes: (i) x, $y-1$, z; (ii) $-x$, $y-3/2$, $-z+1/2$; (iii) x, $-y+3/2$, $z-1/2$; (iv) x, $-y+1/2$, $z-1/2$; (v) x, $y+1$, z; (vi) $-x+1$, $-y+3$, $-z+1$; (vii) $-x+1$, $y+1/2$, $-z+1/2$; (viii) $-x+1$, $-y+2$, $-z+1$; (ix) x, $-y+3/2$, $z+1/2$; (x) $-x$, $y+3/2$, $-z+1/2$; (xi) $-x$, $y+1/2$, $-z+1/2$; (xii) $-x$, $y-1/2$, $-z+1/2$; (xiii) $-x+1$, $y-1/2$, $-z+1/2$; (xiv) $-x$, $-y+2$, $-z+1$; (xv) x, $-y+1/2$, $z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H11···O2^{vi}	0.79 (4)	1.89 (3)	2.6716 (18)	172 (3)
C4—H4···O2^{iii}	0.95	2.52	3.457 (2)	167
C7—H7···O1	0.95	2.28	2.722 (2)	107

Symmetry codes: (iii) x, $-y+3/2$, $z-1/2$; (vi) $-x+1$, $-y+3$, $-z+1$.